

Iridium(I) and Iridium(III) Complexes Supported by a Diphenolate Imidazolyl-Carbene Ligand

David R. Weinberg, Nilay Hazari,[†] Jay A. Labinger,* and John E. Bercaw*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, CA 91125

Supporting Information

HOMO of **8**

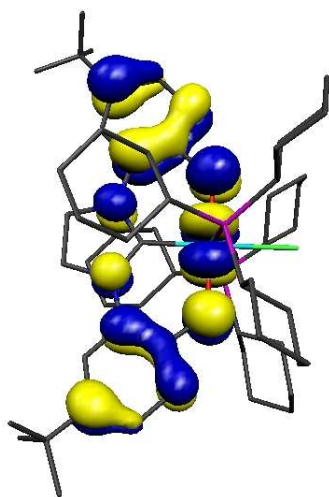


Figure S1. Depiction of the HOMO for the fully optimized gas-phase structure of **8**, determined by QMMM calculations. Hydrogen atoms have been removed for clarity.

Controlled potential electrolysis of **8**

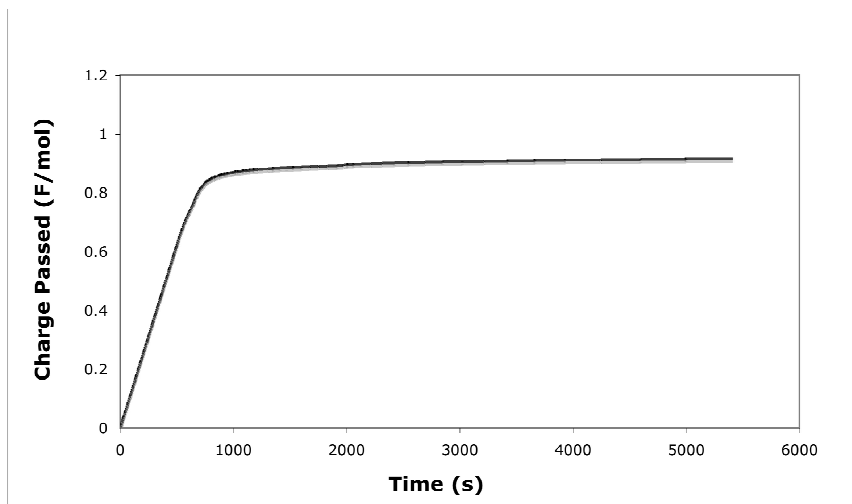


Figure S2. Coulometric oxidation of **8** at a potential positive of the first oxidation wave (0.25 V).

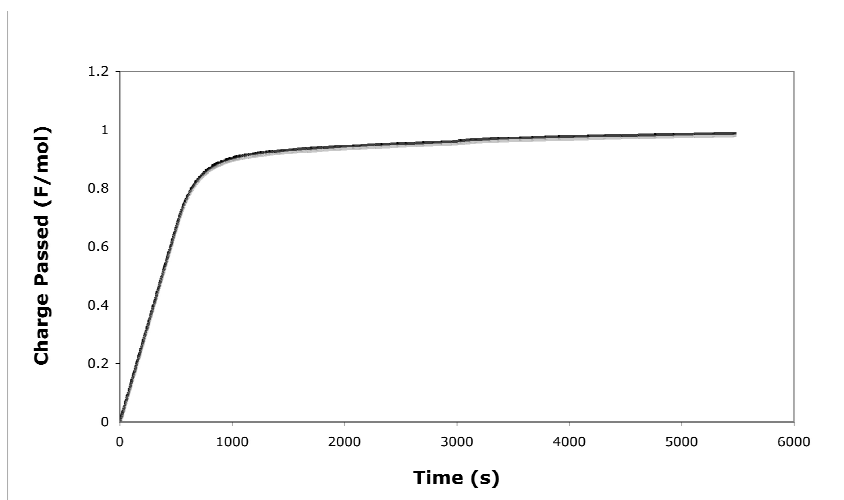


Figure S3. Second coulometric oxidation of **8** at a potential positive of the second oxidation wave of **8** (0.96 V).

Table S1. Selected bond lengths (Å) and angles (°) for **8'**, **8''**, **9**, and **9⁺**.

	Structure			
	8'	8''	9	9⁺
Bond Lengths				
Ir-C15	1.944(2)	1.944(2)	1.95	1.96
Ir-O1	2.0343(16)	2.0307(17)	2.09	2.03
Ir-O2	2.0257(17)	2.0380(18)	2.09	2.03
Ir-P1	2.4365(7)	2.4102(8)	2.34	2.38
Ir-P2	2.4194(7)	2.4260(8)	2.34	2.38
Ir-Cl	2.4584(5)	2.4529(5)	2.49	2.46
Angles				
C15-Ir-O1	93.06(8)	92.75(9)	90.9	92.7
C15-Ir-O2	91.66(8)	90.14(9)	90.9	92.7
C15-Ir-P1	93.67(7)	93.81(8)	97.0	98.8
C15-Ir-P2	94.16(7)	94.60(8)	97.0	98.8
C15-Ir-Cl	179.44(8)	177.33(8)	180.0	180.0
O1-Ir-O2	175.24(6)	177.00(6)	178.3	174.5
O1-Ir-P1	87.51(5)	92.32(5)	87.7	89.6
O1-Ir-P2	88.45(5)	88.27(5)	92.1	89.6
O1-Ir-Cl	87.29(4)	85.42(4)	89.1	87.2
O2-Ir-P1	92.81(5)	86.70(5)	87.7	89.6
O2-Ir-P2	90.58(5)	92.29(6)	92.1	89.6
O2-Ir-Cl	87.99(4)	91.66(4)	89.1	87.2
P1-Ir-P2	171.367(19)	171.53(2)	166.0	162.4
P1-Ir-Cl	86.79(2)	84.32(2)	83.0	81.2
P2-Ir-Cl	85.40(2)	87.30(2)	83.0	81.2
Dihedral Angle				
C _{ipso} -O1-O2-C _{ipso}	-15.72(26)	35.19(26)	-62.6	0.3

XYZ coordinates for optimized structures

9

Ir	-0.000002000	-0.841867000	-0.000001000
Cl	0.000007000	-3.330756000	-0.000004000
P	-0.734832000	-1.126963000	2.198552000
P	0.734856000	-1.126975000	-2.198543000
N	-1.111338000	1.894934000	-0.059702000
C	-2.466071000	1.451744000	-0.076639000
C	-2.808973000	0.100279000	-0.427686000
C	0.763946000	3.321125000	-0.092532000
H	1.059821000	3.679784000	-1.095682000
H	1.286223000	3.930397000	0.661256000
C	2.808967000	0.100287000	0.427691000
C	3.485194000	2.386306000	-0.206477000
H	3.218961000	3.411017000	-0.478663000
C	4.193276000	-0.217971000	0.481964000
H	4.442078000	-1.247203000	0.755183000
C	-3.485202000	2.386300000	0.206472000
H	-3.218971000	3.411013000	0.478650000
H	0.889768000	-0.024664000	-3.107650000
C	5.188332000	0.722967000	0.213436000
H	6.240709000	0.428577000	0.273550000
C	-5.188337000	0.722953000	-0.213424000
H	-6.240715000	0.428560000	-0.273532000
H	-0.889732000	-0.024643000	3.107651000
C	-0.763957000	3.321124000	0.092517000
H	-1.059833000	3.679786000	1.095666000
H	-1.286235000	3.930393000	-0.661273000
C	4.838339000	2.035708000	-0.142329000
H	-2.006464000	-1.758826000	2.345429000
C	-4.838347000	2.035698000	0.142331000
H	0.105307000	-1.981159000	2.972084000
C	-4.193281000	-0.217984000	-0.481951000
H	-4.442082000	-1.247217000	-0.755163000
H	-0.105258000	-1.981186000	-2.972088000
H	2.006496000	-1.758829000	-2.345381000
O	-1.953406000	-0.873361000	-0.737607000
O	1.953402000	-0.873353000	0.737613000
N	1.111330000	1.894936000	0.059691000
C	-0.000004000	1.109555000	-0.000004000
C	2.466064000	1.451749000	0.076636000
H	-5.604426000	2.782717000	0.365415000
H	5.604417000	2.782728000	-0.365414000

9⁺

Ir	-0.000005000	-0.846070000	0.000060000
Cl	-0.000056000	-3.310270000	0.000228000
P	0.003258000	-1.210629000	2.349420000
P	-0.003222000	-1.210944000	-2.349248000
N	-1.112552000	1.905954000	0.000167000
C	-2.461279000	1.489639000	0.000320000
C	-2.845292000	0.096430000	0.002014000
C	0.768537000	3.347856000	0.000442000
H	1.190072000	3.834398000	-0.893283000
H	1.188558000	3.832868000	0.895745000
C	2.845295000	0.096413000	-0.002041000
C	3.476940000	2.475384000	0.000678000
H	3.212989000	3.534043000	0.001979000
C	4.236422000	-0.219727000	-0.002522000
H	4.492183000	-1.282161000	-0.003721000
C	-3.476921000	2.475405000	-0.001016000
H	-3.212963000	3.534061000	-0.002441000
H	-0.003559000	-0.137340000	-3.301308000
C	5.209413000	0.768087000	-0.001329000
H	6.267062000	0.492697000	-0.001613000
C	-5.209407000	0.768119000	0.001164000
H	-6.267058000	0.492737000	0.001457000
H	0.004004000	-0.136896000	3.301335000
C	-0.768513000	3.347860000	-0.000850000
H	-1.190046000	3.834518000	0.892814000
H	-1.188532000	3.832762000	-0.896214000
C	4.827481000	2.127752000	0.000336000
H	-1.109644000	-1.982307000	2.788882000
C	-4.827464000	2.127782000	-0.000661000
H	1.117854000	-1.981424000	2.786157000
C	-4.236422000	-0.219700000	0.002503000
H	-4.492189000	-1.282133000	0.003832000
H	-1.118001000	-1.981472000	-2.785996000
H	1.109496000	-1.983009000	-2.788488000
O	-2.027338000	-0.943860000	0.003136000
O	2.027331000	-0.943872000	-0.003002000
N	1.112567000	1.905947000	-0.000394000
C	0.000006000	1.114309000	-0.000063000
C	2.461293000	1.489624000	-0.000516000
H	-5.584178000	2.915706000	-0.001812000
H	5.584201000	2.915671000	0.001373000

8

P	0.432150000	2.538723000	-0.943994000
Ir	-0.012362000	0.029467000	-0.619710000

P	-0.111893000	-2.476297000	-1.097854000
Cl	0.125215000	0.102417000	-3.144167000
O	-2.043916000	0.330918000	-0.784826000
C	-0.157805000	-0.013045000	1.342171000
C	2.756395000	-0.310078000	0.575950000
C	5.046805000	-0.530715000	1.480564000
H	6.101435000	-0.634805000	1.209551000
C	2.217631000	-2.386747000	-2.825496000
H	1.603713000	-2.595998000	-3.726803000
H	2.252879000	-1.301900000	-2.670290000
C	0.163631000	3.646770000	0.572228000
H	0.320168000	4.698565000	0.261401000
C	1.626219000	-3.091005000	-1.586720000
H	2.286655000	-2.842642000	-0.730130000
C	-2.929075000	0.305700000	0.193198000
C	-0.540997000	3.351827000	-2.364606000
H	0.032267000	3.153459000	-3.293874000
C	4.157834000	-0.448018000	0.410951000
H	4.520263000	-0.487598000	-0.619691000
C	2.278533000	-0.268012000	1.919589000
C	-0.579640000	-3.605190000	0.354464000
H	-0.659024000	-4.640694000	-0.030940000
C	-1.268892000	-2.958612000	-2.529062000
H	-0.684538000	-2.833481000	-3.464276000
C	2.276633000	2.781798000	-1.350691000
H	2.832355000	2.334862000	-0.500187000
N	-1.315851000	0.095116000	2.070099000
C	3.193461000	-0.347858000	2.990011000
H	2.773347000	-0.303315000	3.996223000
C	-2.657963000	0.204757000	1.590154000
N	0.889933000	-0.151964000	2.217429000
C	0.495951000	-3.623220000	1.459999000
H	1.473355000	-3.952539000	1.058114000
H	0.626893000	-2.613443000	1.880344000
C	-5.080633000	0.298126000	2.167958000
C	1.709090000	-4.616613000	-1.814756000
H	1.296410000	-5.182098000	-0.958507000
H	1.153404000	-4.889901000	-2.733178000
C	0.450661000	-0.115685000	3.622922000
H	0.901586000	0.748937000	4.140705000
H	0.770685000	-1.031355000	4.148018000
C	-5.323523000	0.400446000	0.768678000
H	-6.338898000	0.479230000	0.366061000
C	-4.295556000	0.403248000	-0.169087000
H	-4.511088000	0.481198000	-1.238376000
C	3.667486000	-2.828165000	-3.081035000

H	4.040628000	-2.343365000	-4.008858000
H	4.312675000	-2.492044000	-2.239658000
C	-2.504991000	-2.038601000	-2.630972000
H	-3.120713000	-2.103136000	-1.711195000
H	-2.200642000	-0.991243000	-2.762626000
C	3.162872000	-5.058866000	-2.016934000
H	3.757782000	-4.834200000	-1.104178000
H	3.193505000	-6.157192000	-2.184185000
C	-2.332925000	-4.209166000	2.082017000
H	-3.298669000	-3.885410000	2.526957000
H	-2.472727000	-5.230499000	1.664354000
C	3.775966000	-4.348690000	-3.227863000
H	4.845901000	-4.634388000	-3.319554000
H	3.253855000	-4.671435000	-4.155529000
C	-1.271363000	3.539420000	1.114756000
H	-1.467726000	2.508038000	1.431812000
H	-2.012331000	3.797829000	0.337135000
C	1.179663000	3.361374000	1.696815000
H	1.087919000	2.318705000	2.034470000
H	2.217604000	3.511622000	1.341994000
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H	-3.401133000	0.121119000	3.568809000
C	-1.259701000	-4.239339000	3.175798000
H	-1.208877000	-3.250352000	3.678995000
H	-1.535800000	-4.997142000	3.940009000
C	4.591155000	-0.478857000	2.823100000
C	-1.945093000	-3.240790000	0.958649000
H	-1.899245000	-2.228874000	1.374694000
H	-2.741891000	-3.255667000	0.193392000
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H	0.277520000	5.389584000	-2.070764000
C	2.736447000	2.044302000	-2.624799000
H	2.512182000	0.973349000	-2.550777000
H	2.221500000	2.450168000	-3.520971000
C	4.257319000	2.157696000	-2.815678000
H	4.777254000	1.628893000	-1.987056000
H	4.545729000	1.662322000	-3.767776000
C	-1.488409000	4.471383000	2.312500000
H	-1.396107000	5.530051000	1.984129000
H	-2.516042000	4.323911000	2.709402000
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H	-1.590376000	-0.887451000	3.930053000
H	-1.471154000	0.884433000	4.035219000
C	-1.951051000	2.748679000	-2.555733000

H	-1.893769000	1.669035000	-2.749268000
H	-2.571455000	2.899807000	-1.649377000
C	4.713313000	3.619792000	-2.848849000
H	5.822902000	3.658387000	-2.894012000
H	4.315487000	4.112898000	-3.763090000
C	-1.366519000	5.498012000	-3.446658000
H	-0.736956000	5.324743000	-4.347139000
H	-1.468343000	6.595727000	-3.305365000
C	0.960154000	4.291292000	2.896445000
H	1.669023000	4.016477000	3.707179000
H	1.171625000	5.341853000	2.598299000
C	-2.666699000	3.363054000	-3.768047000
H	-2.121632000	3.091051000	-4.698925000
H	-3.692937000	2.942258000	-3.839889000
C	5.518021000	-0.556061000	4.053906000
C	-3.372074000	-2.391821000	-3.848307000
H	-2.802092000	-2.190004000	-4.782129000
H	-4.275538000	-1.744425000	-3.854751000
C	-3.805204000	-3.860013000	-3.821499000
H	-4.489944000	-4.031319000	-2.961698000
H	-4.359819000	-4.097317000	-4.754702000
C	2.706462000	4.260436000	-1.468481000
H	2.263643000	4.709488000	-2.379099000
H	2.395551000	4.849677000	-0.585418000
C	-2.754944000	4.887244000	-3.654894000
H	-3.416477000	5.160429000	-2.803289000
H	-3.203271000	5.300102000	-4.584074000
C	0.112718000	-4.587065000	2.590585000
H	0.099856000	-5.629779000	2.203496000
H	0.877691000	-4.530647000	3.394867000
C	4.229348000	4.372464000	-1.604855000
H	4.513129000	5.443381000	-1.693020000
H	4.722509000	3.960632000	-0.696707000
C	-2.589306000	-4.783349000	-3.705199000
H	-1.959247000	-4.697531000	-4.617821000
H	-2.936891000	-5.836069000	-3.626093000
C	-1.761708000	-4.427307000	-2.465757000
H	-0.928484000	-5.143187000	-2.393257000
H	-2.402340000	-4.589061000	-1.576451000
C	-6.260325000	0.288662000	3.189848000
C	-0.473719000	4.184403000	3.423791000
H	-0.616847000	4.914282000	4.249209000
H	-0.644663000	3.166179000	3.834101000
C	7.007052000	-0.696340000	3.661591000
H	7.175494000	-1.626108000	3.076259000
H	7.649942000	-0.748418000	4.567156000

H	7.341670000	0.177803000	3.062109000
C	5.366761000	0.730055000	4.893895000
H	5.597840000	1.624703000	4.275916000
H	6.059854000	0.716481000	5.762900000
H	4.335766000	0.838386000	5.291163000
C	5.134868000	-1.780414000	4.911999000
H	4.102287000	-1.692036000	5.309914000
H	5.820194000	-1.881688000	5.781386000
H	5.196973000	-2.710960000	4.307190000
C	-6.988596000	1.499496000	3.059156000
H	-6.331504000	2.385127000	3.221420000
H	-7.830135000	1.566203000	3.788490000
H	-7.440652000	1.617078000	2.049455000
C	-5.792905000	0.177761000	4.528094000
H	-5.220015000	-0.764696000	4.688383000
H	-6.627643000	0.169644000	5.268497000
H	-5.132051000	1.030967000	4.806575000
C	-7.101195000	-0.818904000	2.906222000
H	-7.556261000	-0.759011000	1.892713000
H	-7.949634000	-0.899955000	3.626073000
H	-6.533195000	-1.777242000	2.946141000

[†] Current Address: Chemistry Department, Yale University, P.O. Box 208107, New Haven, Connecticut, 06520.